Measurement of glasslike and crystalline elasticity in quasicrystals

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(Received 14 February 1989; revised manuscript received 14 June 1989)

We have measured the Young's modulus and internal friction of several families of aluminumbased quasicrystals from 0.01 to 300 K and from 200 Hz to 8 kHz with a vibrating-reed technique. In the metastable aluminum-transition-metal quasicrystals we see a unique large linear temperature dependence of the internal friction in the 1-100-K range; this is one of the very few measured properties of quasicrystals that differ from metallic glasses or alloys. We do not see the large linear dependence in quasicrystals from the stable families, providing an observable difference in the physical properties of the stable and metastable families. We see glassy behavior in some of the quasicrystals that is as large as that observed in metallic glasses. Finally, we will present lowtemperature speed-of-sound data that cannot be explained by standard models of glasses and alloys.

I. INTRODUCTION

The extremes of order and disorder shape our understanding of solid matter. The theory of crystalline metals and dielectrics is well developed, but our understanding of glasses and other disordered solids is poor. There is a phenomenological model of the surprisingly similar thermal, dielectric, and mechanical properties of these materials below 4 K, and there are some ideas applicable to the 5-100-K range, in which glasses also show similar thermal properties. Nonetheless, there is no coherent picture of the glassy state with anything near the power and clarity that periodicity brings to bear on crystals. In order to identify the kind of disorder that gives rise to the universal properties of glasses and to describe them microscopically, it is important to measure solids possessing various forms of disorder in a progression from pure crystals to completely amorphous materials over a wide range of frequencies and temperatures.

Towards that end, we present in this paper the results of mechanical measurements on vibrating quasicrystal reeds, a class of alloys with a novel structure which is neither translationally periodic nor amorphous. Most of these alloys are cooled more slowly from the melt than metallic glasses, but are cooled much more quickly than crystals, presenting an intermediate state of thermodynamic stability. We have measured the temperature variation of the internal friction, which is the elastic loss experienced by a vibrating solid, as well as the variation in the Young's modulus, which is an elastic constant closely related to the transverse speed of sound. We find that while quasicrystals are essentially crystalline, they can also display unusual mechanical properties.

Birge *et al.*¹ have studied the mechanical properties of reeds of quasicrystals and related alloys between 5 mK and 10 K. In the quasicrystals they find a glasslike elastic signature with a magnitude on the order of one-tenth that seen in metallic glasses. We report here on measurements over a greater variety of alloys and temperatures between 10 mK and 100 K. Although we have seen glassy behavior similar to that seen by Birge *et al.*, we also find elastic behavior below 1 K which is not described by simple glass models, and novel behavior in the activated regime (2-100 K).

Icosahedral alloys, or quasicrystals, were discovered through their remarkable fivefold diffraction patterns. and since then much effort has been exerted to understand the structure of these alloys and to determine the extent and nature of disorder in them.² Investigations of diffraction spot shape and diffuse scattering have helped guide model building in the Penrose tiling³ and randompacking or icosahedral glass traditions.⁴ Just as ordinary crystals have defects and elementary excitations (phonons) corresponding to the breaking of their periodic symmetry, the icosahedral alloys can possess a new kind of distortion, called phasons, corresponding to their classically forbidden symmetries. These phasons are frozen in at the temperatures at which the quasicrystals are stable or metastable, and do not propagate as do phonons in crystals. These phasons can be described as local rearrangements of atoms in icosahedral clusters; this form of disorder and its relationship to the novel symmetry of icosahedral alloys are described elsewhere.⁵⁻⁸

There are several alloy systems in which quasicrystals are now known to occur. Among them are the aluminum-transition-metal (Al-*M*) alloys, discovered by Schechtman⁹ and explored in detail by Bancel.¹⁰ These quasicrystals are metastable; they can be formed only by melt spinning and revert to ordinary polycrystals when heated above a transition temperature. Several other families are stable; both Al-Li-Cu (Ref. 11) and Al-Cu-Fe,¹² for example, can yield large (1-mm) single quasicrystals by conventional casting, with cooling rates on the order of 5 K/min. These large quasicrystals permit "single-crystal" x-ray diffraction.¹³

Diffraction, however, cannot distinguish between stable and metastable quasicrystals, or completely assess the effect of annealing the icosahedral alloys. For example, the correlation lengths of the best Al-M quasicrystals are comparable to those in the macroscopic quasicrystals of the stable alloys, despite the great disparity in their grain sizes. In addition, three quite different thermal treatments of Al-Cu-Fe reveal no appreciable differences in peak position, peak intensity, or lattice parameter, and yield mixed results on linewidths.¹² To better understand these results, and to examine the kinds of disorder which do not show up in diffraction experiments, we have measured the temperature variation of the Young's modulus E and internal friction Q^{-1} of several kinds of icosahedral alloys from 0.01 to 300 K.

We will present a number of unexpected results which bear on the nature of both the quasicrystalline and glassy states. In the aluminum-transition-metal quasicrystals we see a unique large linear temperature dependence of the internal friction in the 1-100-K range. This can be explained by a roughly flat distribution of activation energies of relaxing processes in this range. Such a distribution, although plausible for a disordered metal, is in fact not seen in metallic glasses or alloys at these temperatures. This is one of the very few measured properties of quasicrystals that differ from metallic glasses or alloys. The magnitude of this term can vary with the composition and annealing of the sample, suggesting that it is a consequence of the presence of metastable defects associated with icosahedral ordering. We do not see the large linear dependence in quasicrystals from the stable families. We see glassy signatures in some of the quasicrystals that are as large as those observed in metallic glasses despite the great difference in medium-range order between quasicrystal and glass revealed by x-ray diffraction. Finally, we will present low-temperature speed-of-sound data that cannot be explained by standard models of glasses and alloys.

II. MODELS OF ANELASTICITY

A linear elastic solid obeys Hooke's law, which states that the stress (restoring force) is proportional to strain (displacement from equilibrium) at all times. A linear anelastic solid has an internal degree of freedom, such as the position of a defect, which interacts with strain. This gives rise to a time lag between stress and strain and hence a frequency-dependent loss and elastic modulus. This time, called a relaxation time, is usually denoted by τ , and the magnitude of the effect is A, the relaxation strength. The standard mechanical model for an anelastic solid is a spring in series with a combination of a spring and dashpot in parallel. For this model, the internal friction Q^{-1} and the change in modulus $\delta E/E_0$ are given by

$$Q^{-1} = A \frac{\omega \tau}{1 + \omega^2 \tau^2}$$
 and $\frac{\delta E}{E_0} = -A \frac{1}{1 + \omega^2 \tau^2}$, (1)

where E_0 is the modulus in the limit of no defect motion $(\tau^{-1} \rightarrow 0)$, and ω is the frequency at which the solid is driven (which in our experiments is a resonant frequency of a reed). We will usually discuss our results in terms of a speed of sound $v = \sqrt{E/\rho}$, where ρ is the density. Then $\delta v / v = \frac{1}{2} \delta E / E_0$. It is useful to introduce the derivative with respect to temperature of the relative change in the speed of sound, which we call $\beta \equiv (d/dT)(\delta v / v)$ and will express in ppm/K. Since β is negative for most materials in most temperature regimes (solids get stiffer when cooled), we will also have need of its absolute value $|\beta|$, which we will call the slope. When we say that the slope of $\delta v / v$ is decreasing, we shall always mean that $|\beta|$ is decreasing.

In this section, we review the theory and typical experimental results relevant to each of the possible processes leading to anelasticity. The review will go from wellunderstood and quantitatively useful theories to qualitative explanations, and end with a phenomenon which, while present in a wide variety of disordered systems at easily accessible temperatures, has received very little theoretical attention. The data, to be presented in Sec. IV, will be examined in a similar fashion, progressing from the simplest to the most complicated results.

In crystalline metals, the relevant intrinsic mechanisms are the equation of state of the electron gas and lattice anharmonicity,¹⁴ which give $\delta v/v$ of the form $-A_eT^2 - A_{ph}T^4$ for $T \ll \Theta_D$, where A_e is the electronic contribution, A_{ph} the phonon contribution, and Θ_D is the Debye temperature. In addition, transverse thermal currents induced by inhomogeneous strain during flexural vibration of the reed cause thermoelastic damping. For thermoelastic damping, the terms in Eq. (1) are

$$A = A_{\rm th} \equiv \frac{TE \alpha^2}{C_p}$$
 and $\tau = \tau_{\rm ph} \equiv \left(\frac{t}{\pi}\right)^2 \frac{C_p}{\Lambda}$, (2)

where α is the linear coefficient of thermal expansion, C_p the specific heat, t the sample thickness, and Λ the thermal conductivity. The thermal relaxation time $\tau_{\rm th}$ for a 25- μ m ribbon with the thermal properties of Pd-Si (Ref. 15) at 100 K is calculated to be 3×10^{-5} s. It follows from Eq. (1) that the maximum loss will occur at a frequency of 5 kHz, and that our reed frequencies are not sufficiently far away from this value to allow us to dismiss thermoelastic damping out of hand. For our reeds $A_{\rm th}$ is not negligible compared to other sources of internal friction when $A_{\rm th} > 4 \times 10^{-5}$, which occurs at T > 50 K for most materials in which thermoelastic damping is important. It is difficult to calculate the thermoelastic contribution to Q^{-1} and $\delta v / v$ for our quasicrystals since this requires knowing α , C_p , and Λ as a function of T, as well as a well-defined sample thickness t which in fact can vary substantially around a mean value in the melt-spun quasicrystals. Therefore, instead of trying to compute the thermoelastic effects and subtract them from our data, we looked at Q^{-1} at 100 K at frequencies well below 5 kHz to see if there was a part of \hat{Q}^{-1} which is proportional to ω , and compared it to the part of Q^{-1} which was constant or only weakly dependent on ω . None of the quasicrystals showed an increase in Q^{-1} with ω at 100 K. Therefore, we may ignore thermoelastic contributions to the quasicrystal Q^{-1} below 100 K. The Be-Cu,¹⁶ a low mechanical loss alloy, did show a component of internal friction which was proportional to frequency. Be-Cu and o-Al₆Mn had a Q^{-1} typical for polycrystalline metals without low-energy defects: Q^{-1} was around 2×10^{-4} at 100 K, falling off as a power law in T as α vanishes, reaching a residual value below 15 K. The $\delta v / v$ of these alloys, which will be shown later in Figs. 2 and 5, varies with T in the way a crystal's $\delta v / v$ would, except for a variation of about -10 ppm/K below 15 K. We have concluded that this variation is mostly an artifact of our technique, which requires a glue joint along the line of maximum stress on the reed. Experiments on compound oscillators, in which the joint between a quartz oscillator and the sample is at a plane of zero stress, have shown that annealed Be-Cu shows a $|\beta|$ of at most 2 ppm/K below 15 K.¹⁷ Hence we regard β between -10 ppm/K and 0 for T < 15 K to be indistinguishable from the behavior of a good crystalline material; metallic glasses, in contrast, have β around -100ppm/K in this regime.

Crystals with defects exhibit damping and modulus shifts due to thermally activated processes, such as the Bordoni peak associated with dislocation motion in copper.¹⁸ The relaxation time τ for a defect of activation energy V is $\tau_0 \exp(V/k_B T)$, where τ_0 is a characteristic time of defect motion, on the order of 10^{-13} s in solids. In general, there can be a distribution of activation energies N(V) so that

$$Q^{-1}(T) = A \int \frac{N(V)\omega\tau_0 e^{V/k_B T}}{1 + \omega^2 \tau_0^2 e^{2V/k_B T}} dV ,$$

$$\frac{\delta E(T)}{E_0} = -A \int \frac{N(V)}{1 + \omega^2 \tau_0^2 e^{2V/k_B T}} dV ,$$
 (3)

where E_0 is the elastic modulus at T=0. The relaxation strength A is the average coupling between the activated process and the strain field. In principle, A may be temperature dependent, which complicates the analysis of data taken at a few frequencies as a function of temperature unless N(V) is a very narrow distribution or, ideally, a single δ function. Gilroy and Phillips's analysis¹⁹ of activated defect hopping in a distribution of asymmetric double wells shows how a tempeature-independent A can be theoretically obtained in disordered systems. For narrow features in Q^{-1} , then, we apply the above equations and determine N(V), τ_0 , and A(T). For broad features, we follow Gilroy and Phillips and take A to be constant in temperature to obtain τ_0 and N(V). In amorphous solids, the elastic properties below 1 K are well described by the tunneling-system (TS) phenomenology.²⁰ In this model, groups of atoms in a double-well potential undergo phonon- or electron-assisted transitions between two closely spaced energy levels in response to strain. The potential is characterized by a well asymmetry Δ and a tunneling parameter $\lambda \propto (V_b)^{1/2}$, where V_b is the barrier height between wells. In the standard version of this model, Δ and λ have a flat distribution, giving a nearly flat distribution of energy splittings ε . In normal metallic glasses, the acoustic consequences of this model are $\delta v / v = \frac{1}{2}C \ln T$ and $Q^{-1} = \frac{1}{2}\pi C$, where C is a dimensionless constant defined by

$$C = \frac{\bar{P}\gamma^2}{\rho v^2} , \qquad (4)$$

where \overline{P} is the density of states of tunneling systems, and γ the mean coupling between the energy-level splitting and applied strain. In dielectric glasses, there is a critical temperature T_{co} below which the most rapidly relaxing TS with energy splittings near $k_B T$ have a relaxation time greater than the period of the applied strain. Then $\delta v / v = C \ln T$ for $T < T_{co}$ and $\delta v / v = -\frac{1}{2}C \ln T$ for $T > T_{co}$. For almost all amorphous solids, various experimental techniques show that T_{co} is around 50 mK at 1 kHz and is proportional to $\omega^{1/3}$. Similarly, $Q^{-1} = \frac{1}{2}\pi C$ as for metallic glasses for $T > T_{co}$, but the theory predicts that Q^{-1} should vanish as T^3 for $T < T_{co}$. This temperature and frequency dependence of Q^{-1} has been observed in ultrasonic experiments with several amorphous solids. Elastic properties at lower frequecies, measured with mechanical oscillators, show that T_{co} varies with frequency as predicted²⁰ down to 1 kHz, and that the internal friction varies as T^3 for $T \ll T_{co}$ at frequencies as low as 66 kHz.²¹ The behavior of superconducting metallic glasses is more complicated as it involves accounting for the strong coupling of the electrons to the TS as well as the rapid variation in the quasiparticle density of states near and below the transition temperature T_c . At $T \ll T_c$ the electrons are frozen out and the elastic properties of superconducting metallic glasses are qualitatively similar to those of dielectric glasses. We will refer to a physical property as glasslike if its T dependence roughly follows the dependences just described, and when we say C is small, we will mean that it is less than 10^{-5} , which is roughly ten times smaller than the C of the metallic glasses PdSi or CuZr as measured at similar frequencies.

Spin glasses possess another kind of disorder, the elastic behavior of which is at least qualitatively understood; this is seen most clearly in work on the CuMn system²² (where the notation denotes a dilute solution of magnetically active ions in a host metal). Because of the full miscibility of Mn in Cu, CuMn can be grown as nearly defect-free single crystals, thereby eliminating phenomena arising from structural disorder or other defects. Then departures from the crystalline behavior of $\delta v / v$ and Q^{-1} can be attributed unambiguously to the spin interactions. Experiments^{23,22} on the spin glasses $Fe_{50}Ni_{21}Cr_{20}$ and CuMn have shown a contribution to $\delta v / v$ that is proportional to the real part of the susceptibility but of opposite sign; the magnetic interactions soften the crystal by a few parts per thousand near the spin-glass transition temperature T_g . The magnitude of this contribution is a maximum at T_g and is proportional to T for $T \ll T_g$ and proportional to 1/T for $T \gg T_g$. This proportionality is suggested by theory,^{24,25} although it is difficult to get an accurate number for the constant of proportionality. Theory also suggests that for spin glasses Q^{-1} is proportional to the imaginary part of the susceptibility; the existing data are less convincing on this point.

Finally, we come to a phenomenon which occurs in all metallic glasses and many disordered dielectrics, such as amorphous Se-Ge compounds, which was first noted by Bellessa.^{26,27} which we will call the Bellessa effect. In crystals, the speed of sound ceases to change at low temperatures as the anharmonic effects and defect motion are frozen out. In glasses, on the other hand, the sound velocity at frequencies up to 450 MHz is observed to increase linearly as the temperature is decreased from 25 to 4 K. This variation is in marked disagreement with the observed internal friction and the relationship between modulus change and internal friction given by Eq. (1). This effect has also been seen in metastable alloys with long-range crystalline order,²⁸ and the relationship between TS and the Bellessa effect in such solids remains an area of active work and lively speculation.²⁹

One way to explain this term is to modify the flat distribution of tunneling parameters and well asymmetries in the standard tunneling model to give more states at large tunneling parameters (large barriers or well separations) than at low barrier heights,³⁰ an approach which has been faulted for not explaining the physics behind the additional parameters,²⁰ or for not explaining both frequency and temperature dependences at the same time.^{26,27} A resolution of this issue is beyond the scope of this paper. It cannot be explained by retaining the flat distribution and adding higher-order terms such as twophonon processes to the relaxation of tunneling systems; this transforms the $\ln T$ dependence of the speed of sound on temperature to a logarithm of a polynomial in T, which will change the coefficient but will have a small effect on the functional form of this dependence over a limited temperature range. By using the tunneling-state densities inferred from the low-temperature internal friction as well as typical couplings for these higher-order processes, we can mimic the linearity but not the magnitude of the Bellessa effect over the full measured temperature range;³¹ we can get a pseudolinear $\delta v / v$ with a β of only -10 ppm/K. Although the TS theory is usable at kHz frequencies even if the linewidths are comparable to ε for states with $\varepsilon \approx k_B T$ —as in normal metallic glasses below 2 K-above 30 K phonons would relax tunneling systems so rapidly that their intrinsic linewidths would be much larger than $k_B T$, suggesting that the concepts useful below 1 K must be significantly revised in the intermediate temperature regime (2-100 K). The temperature range of the Bellessa effect is too low for anharmonic effects and other fundamental processes³² to contribute (as discussed above), and activated processes which can explain Q^{-1} at these temperatures can account for only a

small part of $\delta v / v$. This mystery is particularly stark in the case of metallic glasses like Pd-Si and Cu-Zr, in which the temperature independent Q^{-1} in this region can be accounted for with the same TS which explain the <1-K elastic properties. Then there are no activated processes needed to explain Q^{-1} , but one observes β of -100 ppm/K!

When we turn to the data (Sec. IV) we will see which of these processes which occur in familiar alloys can also occur in this new class of alloys, quasicrystals.

III. EXPERIMENTAL PROCEDURE

Our quasicrystals are melt-spun by induction melting a piece of a drop-cast arc-melted master alloy in a quartz tube with a nozzle diameter of roughly 0.5 mm; the melt is forced out by 1.3 bar of argon onto a 30-cm-diameter copper wheel spinning at roughly 2000 revolutions per minute a few millimeters from the nozzle. This produces brittle ribbons typically 1 cm long, 1-2 mm wide, and 25 μ m thick. These ribbons were characterized by x-ray diffraction, transmission electron microscopy, electron diffraction, energy-dispersive elemental analysis, inductively coupled plasma analysis, differential scanning calorimetry, and by the examination of defect-etched ribbons in a scanning electron microscope. Most quasicrystals measured had less than 5% of intruding phases, and consisted of dendritic regions between 1 and 10 μ m in diameter. Selected area electron diffraction showed orientational order to be maintained over these regions. We measured the Al-M quasicrystals Al₈₀Mn₂₀, Al₇₉Ru₂₁, $Al_{76}Mn_{17}Ru_4Si_3$, $Al_{78}Cr_{17}Ru_5$, and $Al_{75}Re_{21}$, Si_4 , as well as $Al_{65}Cu_{20}Fe_{15}$ and $Al_{57}Li_{33}Cu_{10}$. We compared these to orthorhombic Al_6Mn (o- Al_6Mn), the decagonal phase³³ T-Al₇Mn₂, the metallic glass Pd-Si, and annealed Be-Cu, a low-loss commercial alloy of mixed crystalline phases.

We measured the elastic properties with a vibrating reed technique. The end of a reed was wet with Stycast 2850 quartz-filled Epoxy or Eccobond silver Epoxy³⁴ and clamped in a brass pedestal. A typical reed had a fundamental frequency of 250 to 400 Hz. Its resonant frequency is proportional to the sound velocity v determined by the Young's modulus E^{35} :

$$v \equiv \left(\frac{E}{\rho}\right)^{1/2} = v_t \left(\frac{3v_t^2 - 4v_t^2}{v_t^2 - v_t^2}\right)^{1/2}$$
$$= v_t \left(3 - \frac{v_t^2}{v_t^2 - v_t^2}\right)^{1/2}, \qquad (5)$$

where v_t and v_l are the transverse and longitudinal speeds of sound. Since v_l^2/v_t^2 is between 2.5 and 3 for most solids, we assume $v \approx 1.6v_t$. To study the frequency dependence of the elastic properties, we excited the overtones of flexural vibration near 6 and 17 times the fundamental frequency. If this was not possible because of weak coupling to the electrodes or irregular sample shape, we clipped the reeds to raise their fundamental frequency. It was often useful to do both: to measure a fundamental and overtone, then clip the reed so that the new fundamental frequency was roughly equal to that of the overtone of the unclipped reed. This is important because the mode shapes of a beam in flexure are different for different modes. For example, the maxima of stress and strain in the fundamental mode occur at the base of the reed, while for the second mode, there are two maxima, one at the base and one at a point halfway up the reed.¹⁸ If the elastic properties at the center of the reed are different from those at the clamped end, data taken on different overtones of the same reed could lead one to mistake an inhomogeneity effect for a spurious frequency dependence of the elastic properties. Clipping the reed in the manner described thus allows us to distinguish genuine frequency dependences from the effects of inhomogeneity, as we will discuss along with our results on the Al-M alloys.

For each sample, we measured tuning curves at different driving amplitudes to establish the calibration of Q versus signal amplitude and driving voltage. Some of the reeds showed nonlinearities in the elastic modulus of up to one part in 10⁴ for a factor-of-2 change in amplitude at their operating amplitude. None of the reeds exhibited nonlinearity in their internal friction over the range of amplitudes which we used in our experiments. To accurately establish the calibration of O versus amplitude, the measured tuning curves were used to correct for these small nonlinearities. As the temperature was varied, a phase-locked loop was used to track the resonant frequency, and a computer-controlled drive voltage maintained a constant strain amplitude between 10^{-5} and 10^{-7} . We were able to measure changes in frequency to better than one part in 300Q (about one part per million at low temperatures), and Q^{-1} to a few percent. From the lowest observed Q^{-1} on crystalline samples with the same geometry as the quasicrystals (o-Al₆Mn) we conclude that the clamping loss for all samples is less than 2×10^{-5} below 10 K.

Self-heating of the samples from internal friction was not a problem at the amplitudes and temperatures used in this study. This was checked at 85 mK for $Al_{76}Mn_{17}Ru_4Si_3$ and at 13 mK for the $Al_{79}Ru_{21}$. In the latter case, the Q^{-1} versus T curve at fixed amplitude was used to establish that there was a self-heating of 2 mK at the highest amplitude used in the fixed-amplitude scans of Q^{-1} and $\delta v / v$ versus T. Since thermal resistances drop rapidly as T increases at these temperatures, self-heating was, in general, a negligible effect. A calculation for a typical reed³⁶ with a Q of 5000 which assumes boundary-resistance limited heat transfer gives a selfheating of 2 mK at 30 mK for a strain of 10^{-6} , in good agreement with the Al₇₉Ru₂₁ results considering the variability of thermal boundary resistances and the difficulty of accurately calculating the constant of proportionality between reed vibration amplitude and signal strength.

Because of thermal contraction and the large variation in elastic constants over the wide range of temperatures reported here, it is important to eliminate measurement artifacts. For example, the electrical coupling between the electrodes and the reed can change if the reed rotates in its joint during cooling. Changes in the coupling of the reed to the electrodes can be accounted for by measuring the linewidth of the resonance and comparing it to the height of the peak at various temperatures. Another possible consequence of joint rotation is a spurious electrostatic softening of the reed.¹⁵ The presence of this artifact is detected by measuring the magnitude of the frequency dependence of the resonance on the square of the bias voltage. We compare typical values for the variation of the speed of sound with temperature for known alloys with the temperature variation of the electrostatic softening at the measurement bias. Practically, if the electrostatic term is larger than 5% of the typical intrinsic term we reject the sample mounting and readjust the electrodes. All of these artifacts are checked by verifying the known elastic properties of such materials as annealed BeCu and PdSi with the same mounting scheme used with the quasicrystals.

We checked the reproducibility of our data by running several reeds of the same spinning for different families of alloys. The most reproducible were the Al-Cu-Fe reeds, which showed less than 10% variation in Q^{-1} and $\delta v / v$ at a given temperature. The most variable were the Al-M alloys which contained manganese. Reeds of as-spun Al₇₆Mn₁₇Ru₄Si₃, for example, could have a Q^{-1} between 3.0×10^{-4} and 4.1×10^{-4} at 5 K. Despite the quantitative differences, we observed no qualitative differences in the measured temperature dependences of Q^{-1} and $\delta v / v$ between reeds of the same composition produced in different spinnings with the same wheel speed. Repeated runs of the same sample in the same pedestal were reproducible within a few percent over at least a year.

IV. EXPERIMENTAL RESULTS AND DISCUSSION OF DATA

Figure 1 shows the internal friction Q^{-1} from 2 to 100 K, Fig. 2 shows the relative change in the speed of sound $\delta v / v$ in the same temperature range, and Figs. 3 and 4 illustrate the behavior of some quasicrystals and other alloys below 5 K. We will group them by similarities in Q^{-1} and $\delta v / v$ and explain the shared features using the ideas outlined in Sec. II, as we progress from the simplest to the most complicated cases.

The quasicrystal that most resembles ordered crystals is the stable phase $Al_{57}Li_{33}$ Cu₁₀, which is compared with Be-Cu and the metallic glass Pd-Si in Figs. 5 and 6. Q^{-1} is comparable to that of Be-Cu or o-Al₆Mn at 100 K, and falls asymptotically to 3×10^{-5} , which is much less than that of a typical glass (10^{-4}) . Also, neglecting a residual β of -10 ppm/K which we believe to be an experimental artifact, we do not see the linear variation with T in $\delta v / v$ which appears in all metallic glasses measured in this regime.²⁰ Figure 5 shows how $\delta v / v$ for Al₅₇Li₃₃Cu₁₀ resembles the results for BeCu rather than those for the metallic glass Pd-Si. Figure 6 shows how Q^{-1} for $Al_{57}Li_{33}Cu_{10}$ compares to the polycrystal and the metallic glass. This low level of disorder is manifest in the TS regime below 1 K as well, as shown by the results on Al-Li-Cu of Birge et al.¹. Hence it seems that the level of intrinsic disorder in these quasicrystals is much less than that in metallic glasses.

The Al₆₅Cu₂₀Fe₁₅ shows more loss and greater $\delta v / v$.



FIG. 1. Internal friction Q^{-1} vs temperature for several icosahedral alloys compared to o-Al₆Mn and T-Al₇Mn₂. All samples are melt-spun ribbons, with first mode resonant frequencies between 250 and 400 Hz. Symbols and lines are based on data points separated by 2 K or 10% of T, whichever is less. Good quasicrystals, such as Al₅₇Li₃₃Cu₁₀, are essentially crystalline in their elastic properties. The linear temperature dependence of Q^{-1} for some of the Al-M quasicrystals has not been seen in other metals. The Q^{-1} of the Al-M quasicrystals varied from sample to sample of a given melt spinning by the extent of the bar shown for Al₇₆Mn₁₇Ru₄Si₃; for the other alloys, the variations were less than half as large (less than 10%).

Although Q^{-1} is the same as that of Be-Cu and Al₅₇Li₃₃Cu₁₀ at 100 K, Fig. 1, it falls off more slowly below 70 K and is nearly constant at 8×10^{-5} below 2 K, Fig. 3. There is a Bellessa term of $\beta = -40$ ppm/K, Fig. 2. Although no one has yet done a systematic study of the relationship of this linear variation of $\delta v / v$ with T to the magnitude of the TS effects in metals,



FIG. 2. Temperature-dependent change in speed of sound $\delta v/v$ vs T for the icosahedral alloys shown in Fig. 1 and $o-Al_6Mn$. For most glasses, $\delta v/v \propto -T$ between 2 and 30 K, while for crystals $\delta v/v$ vanishes as $-T^4$. $\delta v/v$ for different samples are offset for clarity. Note the resemblance between $o-Al_6Mn$ and $Al_{57}Li_{33}Cu_{10}$ and the similarity of the Al-Cu-Fe and Al-Cr-Ru curves.



FIG. 3. Internal friction Q^{-1} of icosahedral alloys, the superconducting metallic glass Cu-Zr (Ref. 15), and the normal metallic glass Pd-Si. The Al₇₉Ru₂₁ shows a glasslike signature twice as large as Cu-Zr; for the other quasicrystals internal frictions between 2×10^{-5} and 2×10^{-4} persist to the lowest temperatures measured.

Raychaudhuri's²⁰ work on metallic glasses suggests that a Bellessa term of the size is comparable to that of metallic glasses which have a TS coupling C near 5×10^{-5} . Such a coupling would give the correct Q^{-1} below 1 K and predict a $\delta v / v = 3 \times 10^{-5} \ln T$ in that temperature range. The low-temperature data on Al₆₅Cu₂₀Fe₁₅, however, do not show this behavior, but rather have a minimum in $\delta v / v$ near 0.6 K, Fig. 4, and a β of -36 ppm/K below



FIG. 4. Relative change in $\delta v / v$ vs ln*T* for icosahedral alloys, the superconducting metallic glass Cu-Zr, and the normal metallic glass Pd-Si. The resonant frequency is 750 Hz for Al₇₉Ru₂₁ and 1600 Hz for Cu-Zr. The speed of sound variations for Al₇₉Ru₂₁ and Cu-Zr agree with the results in Fig. 3, while the result for Al₇₅Re₂₁Si₄ are smaller in magnitude but qualitatively similar to that of Pd-Si. Quasicrystals containing the magnetic atoms Mn or Fe are qualitatively different from these alloys in their speed of sound variation below 1 K. $\delta v / v$ have been scaled by the factors noted to permit comparison of signatures on the same graph.



FIG. 5. Temperature variation of the speed of sound in the $Al_{57}Li_{33}Cu_{10}$ quasicrystal and two well-characterized metals: the metallic glass Pd-Si and annealed Be-Cu, which is a finegrained mixture of two crystalline phases. Al-Li-Cu is much more like the polycrystal than the metallic glass.

0.3 K. This is more like the behavior of a spin glass with T_g near 0.6 K, and β for $T \ll T_g$ is comparable to -20 ppm/K found for $CuMn^{22}$. The glassy signatures below 1 K may be masked if magnetic moments or other defects are present, and a reliance on only the data below 1 K may lead to contradictory results. Here we use the data above 1 K to conclude that $Al_{65}Cu_{20}Fe_{15}$ has few activated defects, but is less ordered than $Al_{57}Li_{33}Cu_{10}$. The absence of any lnT term in $\delta v / v$ down to 20 mK suggests, however, that the TS constant is much smaller than what can be estimated from the residual damping. The $Al_{65}Cu_{20}Fe_{15}$ therefore appears to be more disordered than the $Al_{57}Li_{33}Cu_{10}$, but not yet glasslike.

The decagonal- or T-phase $T-Al_7Mn_2$ is quasiperiodic in two dimensions and periodic in the third. Figure 1



FIG. 6. Internal friction for $Al_{57}Li_{33}Cu_{10}$, Pd-Si, and Be-Cu, showing the distinction between the internal friction of polycrystals and metallic glasses at low temperatures. Note that this graph shows only the lowest fifth of the internal friction range of Fig. 1.

shows that it has a relatively simple spectrum of activated processes, compared to the Al-M quasicrystals. A peak of height 1.4×10^{-4} rises from this background near 30 K at kHz frequencies. There is a background damping of 1.2×10^{-4} and a frequency-independent linear variation in $\delta v / v$ with T of roughly -40 ppm/K. The frequency dependence of the peak and the dispersion of $\delta v / v$, Fig. 7, in this temperature range can be explained by activated processes with $\tau_0=2\times 10^{-12}$ s and a distribution of activation energies which is sharply peaked near $V/k_B = 500$ K, and has a flat tail of lower-energy excitations extending to energies as low as $V/k_B = 250$ K. We conclude that the T phase has even more disorder than Al₆₅Cu₂₀Fe₁₅, as well as activated processes not found in the two quasicrystals already mentioned.

Our final family of quasicrystals, the Al-M family, is the most diverse. Those without magnetic moments, such as Al₇₉Ru₂₁ or Al₇₅Re₂₁,Si₄, exhibit glassy behavior below 1 K. Those containing manganese have a $\delta v / v$ which resembles that of spin glasses^{$\overline{2}2$} between 1 and 20 K. The most remarkable feature of this family, however, is common to all of these alloys: a Q^{-1} which varies almost linearly with T between 2 and 100 K, as shown in Fig. 1. This variation of Q^{-1} with T is not seen in other metals, and is one of the few experimental results on quasicrystals, besides diffraction, in which they show themselves to be different from either polycrystals or metallic glasses. As in the amorphous solids studied by Raychaudhuri or Bellessa, the distribution of activation energies which accounts for Q^{-1} explains only a part of the temperature variation of $\delta v / v$. First we will examine the elastic behavior of alloys in this family that can be attributed to familiar processes. Then we will describe the novel internal friction which can occur in this family.

 $Al_{79}Ru_{21}$, for example, behaves similar to a superconducting metallic glass. We measured the Meissner effect by embedding 20 mg of powdered alloy in an epoxy pill with fine Cu wires for heat sinking and placing it in one-



FIG. 7. The dispersive part of the speed of sound variation for the decagonal phase $T-Al_7Mn_2$. A background of -40 ppm/K has been subtracted and the results for the first two modes of the reed at 560 and 3300 Hz are set equal at 40 K, well above the internal friction peak shown in Fig. 1.

half of an astatic coil pair. The mutual inductance signal at 1 kHz and a few gauss showed flux expulsion from most of the sample volume with the midpoint of the transition at 0.8 K with a 10-90 % width of 0.2 K. The elastic measurements, Figs. 4 and 3, show a $\delta v/v$ which peaks at 35 mK at 800 Hz and a Q^{-1} which is nearly constant down to this temperature and decreases rapidly as T is reduced still further. For comparison, we show results on Cu-Zr, a superconducting metallic glass with T_c around 0.3 K, which also has these features. In $Al_{79}Ru_{21}$, the magnitudes of the $\ln T$ term in $\delta v / v$ and Q^{-1} above 50 mK are twice the size of the corresponding quantities in Cu-Zr, confirming that TS are as common in this quasicrystal as in a typical metallic glass. This does not imply that $Al_{79}Ru_{21}$ is a metallic glass, however. As the studies of recrystallized Pd-Si by Cibuzar et al.³⁷ have demonstrated, it is possible to produce samples which show the x-ray patterns of polycrystalline alloys but have the same TS coupling C, observed through elastic measurements, as amorphous metals. Similarly, x-ray powder patterns of the $Al_{79}Ru_{21}$ show that although the composition is mostly quasicrystal with a few percent fcc Al, it exhibits full glassy elastic behavior.

In $Al_{75}Re_{21}Si_4$ we have somewhat less agreement with the TS picture. Although β is positive below 1 K, the data is equally poorly fit by $\ln T$ or T between 0.02 and 1 K. We determined that the low-temperature limits of $\delta v / v$ and Q^{-1} are not caused by self-heating of the reed, as explained in Sec. III. We have found that the magnitude of this frequency variation below 1 K is inversely proportional to the amplitude of vibration, while the TS model predicts no amplitude dependence of elastic properties at these frequencies. Nevertheless, since both spinglass and relaxational (both TS and activated) interactions should give a negative β as $T \rightarrow 0$, according to theory, we can still conclude that there are resonant interactions with defects similar to, but not identical with, those found in metallic glasses. Q^{-1} at 1 K is ten times larger than that of $Al_{57}Li_{33}Cu_{10}$, Fig. 3.

The third nonmagnetic alloy in this family is Al₇₈Cr₁₇Ru₅. Although we have not measured its properties below 1 K, $|\beta|$ is less than 25 ppm/K between 1.5 and 4 K, Fig. 8, just as is the case for $Al_{75}Re_{21}Si_4$ and Al₇₉Ru₂₁, and quite unlike the behavior of the Al-M alloys which contain Mn. This implies that the low T propeties of Al₇₈Cr₁₇Ru₅ are similar to those of Al₇₅Re₂₁Si₄ and $Al_{79}Ru_{21}$. The Q^{-1} is the lowest of any nonmagnetic Al-M alloy we have measured, and the characterization steps discussed in Sec. III revealed large grain size and low levels of other phases. Hence we will use the Al₇₈Cr₁₇Ru₅ as a standard against which to compare the more complicated behavior of the manganese alloys in our discussions of the spinglass contribution, Fig. 8. Since its Q^{-1} is in the middle of the range spanned by all the Al-M alloys, magnetic and nonmagnetic, we will also return to Al₇₈Cr₁₇Ru₅ in our discussion of the Bellessa effect in these alloys, Fig. 9.

The Al-M alloys containing Mn do not show any features in agreement with the TS picture. The temperature coefficient β is large and negative below 1 K



FIG. 8. Qualitative effect of spin-glass interactions on $\delta v / v$ of an Al-M quasicrystal. We choose a linear combination of the $\delta v / v$ of Al₇₈Cr₁₇Ru₅ and the magnetic susceptibility of Al-Mn-Si as measured by Eibschütz *et al.* (Ref. 38). This linear combination matches the temperature derivative of the relative change in speed of sound at 1 and 10 K and produces the spinglass curve. This curve qualitatively reproduces the curvature and $T \rightarrow 0$ limit of the $\delta v / v$ data below 10 K which are found in the magnetic Al-M quasicrystals but which are absent in the nonmagnetic members of this family.

 $(\approx -300 \text{ ppm/K})$, while Q^{-1} drops by a third between 1 and 0.02 K, see Fig. 3. Unlike all the other quasicrystals, for which $|\beta| < 25 \text{ ppm/K}$ between 1 and 4 K, $|\beta|$ remains large (100 ppm/K). Above 4 K, the slope increases again to 175 ppm/K at 6 K.

In Fig. 8 we present an expanded view of $\delta v / v$ for $Al_{76}Mn_{17}Ru_4Si_3$, which shows the features below 10 K which we will now explain as a consequence of magnetic interactions. In one of the first studies of the elasticity of spin glasses²², performed on CuMn, the procedure was to subtract a background $\delta v / v$ based on the functional form expected for an otherwise perfect crystal, using measure-



FIG. 9. Disagreement between the experimental $\delta v / v$ and the $\delta v / v$ calculated from a distribution of activated processes which fits the internal friction, for Al₇₈Cr₁₇Ru₅. The difference is a common feature of disordered materials between 2 and 30 K, especially in metallic glasses.

ments of $\delta v / v$ at $T \gg T_g$, in this case 30-70 K, and to establish the constant of proportionality between the remaining change in modulus and the magnetic susceptibility χ , as suggested by theory. Since CuMn can be grown as large single crystals, the contribution of structural disorder to elastic behavior may plausibly be neglected. In the case of Al₇₆Mn₁₇Ru₄Si₃, however, we do not have a quantitative idea of what the background is—it could include activated processes, a term linear in T as discussed by Bellessa,^{26,27} and the anharmonic effects seen in crystals as well. Instead, we try to understand it by referring to $Al_{79}Ru_{21}$, $Al_{75}Re_{21}Si_4$, and $Al_{78}Cr_{17}Ru_5$. For example, we made a linear combination of $\delta v / v$ for $Al_{78}Cr_{17}Ru_5$ and the χ of $Al_{74}Mn_{20}Si_6$ quasicrystals measured by Eibschütz et al.³⁸ We chose the constants of proportionality to give the measured β of Al₇₆Mn₁₇Ru₄Si₃ at 1 and 10 K. The result is the solid line shown in Fig. 8, labeled "spin glass." This reproduces the qualitative features of the alloys containing Mn. An understanding of the Mn alloys below 5 K, including the dramatic changes below 30 mK observed by Haemmerle et al.,³ will require further work on crystalline and amorphous spin glasses.

While their low-temperature properties are diverse, the Al-M alloys are similar in Q^{-1} and $\delta v / v$ above 10 K: Q^{-1} varies roughly linearly with T with finite damping as $T \rightarrow 0$. This linear temperature dependence is unusual, and has not been seen in any other metallic system, crystalline or glassy. The magnitude of this linear term can vary by a factor of 4 between different samples of similar composition; for example, we have made samples of Al₇₄Mn₂₀Si₆ for which the Q^{-1} is one-fourth that of Al₇₆Mn₁₇Ru₄Si₃ in the 1 to 100 K range.

Although this term is of variable magnitude, we are convinced that it is not an artifact of our measurement, but is instead a novel form of internal friction which occurs under certain conditions in these metastable quasicrystals. Through careful characterization we have eliminated the complex morphology of these samples as a source of the anomalous internal friction. We have seen similar magnitudes of this effect in quasicrystals with grain sizes ranging from below 1 μ m to greater than 10 μ m. The stable phase quasicrystals that we have measured do not show this behavior, although they have similar grain sizes and gross morphology, and are meltspun under identical conditions. We have made a metastable crystalline solid solution, Al₉₅Mn₅, which does not show this effect, and we do not see it in the metallic glass $Pd_{80}Si_{20}$. The fundamental losses in our apparatus have been carefully characterized by measuring the elastic properties of the annealed polycrystal Be-Cu in a compound oscillator, Be-Cu glued into a pedestal as a reed, and of reeds made entirely of Stycast 2850FT. From these data we conclude that the mounting scheme does not contribute in a substantial way to the elastic properties of the quasicrystals. We have noted, however, that annealing can reduce the magnitude of this linear term. The quasicrystal Al₇₆Mn₁₇Ru₄Si₃ was annealed for 24 h at 523 K in vacuum, a temperature chosen to be slightly below the onset of the metastable transition as determined by differential scanning calorimetry. Following

this treatment it showed a 50% reduction in both Q^{-1} and the Bellessa term. This observation suggests that the origin of this unusual internal friction is disorder that was quenched in as these quasicrystals were formed; its absence in the more stable families of quasicrystals (Al-Cu-Fe, Al-Li-Cu) suggests its relationship to the kinetics of growth.

Studies of the higher modes of the Al-M reeds indicate substantial inhomogeneity effects in some of the samples. Variations in sample thickness cannot produce inhomogeneity effects; they are rather a local property of the solid. The Al₇₄Mn₂₀Si₆ reed, for example, showed a Q^{-1} at 40 K of 1.5×10^{-4} for the fundamental at 110 Hz and a Q^{-1} of 2.4×10⁻⁴ for the second mode at 600 Hz, an implausibly rapid variation with frequency compared to the $\ln \omega$ dependence expected for either activated processes or TS. When the reed was clipped to raise the fundamental mode to 430 Hz, Q^{-1} was 1.5×10^{-4} . Since the points of maximum strain in the fundamental mode are the base of the reed, and at the base and the point halfway up the reed in the second mode, the unusual frequency behavior of the original reed can be attributed to higher damping at the reed center than at the clamped end, rather than to any intrinsic variation with frequency. This example shows the importance of cross checking any unusual frequency dependences in elasticity data obtained by the vibrating reed technique; one must compare several samples at the same frequency, or obtain similar frequencies on the same reed by the two different methods of exciting a higher tone or clipping the reed.

Since the unusual linear Q^{-1} is not peaked, there is a broad distribution of activation energies, and we will assume the material is disordered to the extent that Gilroy and Phillips's deduction of a temperature-independent relaxation strength A is valid.¹⁹ If we make N(V) in Eq. (3) the step distribution $N(V) = \overline{N}$ for $V < V_{\text{max}}$ and N = 0for $V > V_{\text{max}}$ and look at $T \ll V_{\text{max}}/k_B$, then Q^{-1} $= \frac{1}{2}\pi A \overline{N} k_B T$ and

$$\frac{\delta v}{v} = \frac{1}{2} \frac{\delta E}{E_0} = -\frac{1}{2} A \overline{N} k_B T \ln(1/\omega\tau_0) \approx -10 A \overline{N} k_B T \qquad (6)$$

for kHz frequencies and typical τ_0 . More generally, if $N \propto V^n$, then $Q^{-1} \propto T^{n+1}$ and $\Delta E / E_0 \propto -T^{n+1}$. The temperature-dependent part of the Q^{-1} for these quasicrystals can be fit by *n* between -0.5 and 0. Such a flat distribution is physically plausible in a disordered system; it is surprising that it has not been seen in other disordered materials.

The temperature at which damping is observed can be converted to an activation energy by noting that $\omega \tau = 1$ at the center of the resonance, and $V = k_B T \ln(1/\omega \tau_0)$ relates the energy V to the temperature T at which damping is seen at frequency ω . With a typical τ_0 of 10^{-13} s, then, we get a range of activation energies that is roughly flat from at least 0.004 to 0.2 eV. This range of energies is unusual. For comparison, in vitreous silica¹⁹ $N(V) \propto \exp(-V/V_0)$ with $V_0 \approx 0.05$ eV. Excitations that have characteristic energies in this range include small-angle bond bending in a covalent glass (≈ 0.05 eV) and the Bordoni peak associated with dislocation motion $(\approx 0.12 \text{ eV})$. Diffusive processes occur at higher energies $(\approx 1 \text{ eV})$.

As in other disordered metals and dielectrics, the distribution of activation energies needed to describe Q^{-1} leaves much of $\delta v / v$ unaccounted for. Figure 9 shows an example that of Al₇₈Cr₁₇Ru₅; it compares the measured $\delta v / v$ with that calculated from the distribution of activated processes used to fit Q^{-1} . The difference between them is roughly linear between 10 and 50 K, as found in previous work, with a slope between 50 and 190 ppm/K for different quasicrystals, typical of the values found in metallic glasses. This slope is roughly proportional to Q^{-1} at 1 K. This is remarkable, suggesting that $T \rightarrow 0$ damping is related to the linear variation of $\delta v / v$ with T which remains after the speed of sound contribution of the activated processes has been accounted for. The connection with TS theory is, however, obscured by occasional disagreement²⁰ in the values of C obtained from measurements of $\delta v / v$ or Q^{-1} .

V. CONCLUSIONS

We have observed a wide variety of elastic behavior in quasicrystals: the temperature variation of Q^{-1} and $\delta v / v$ for various samples and temperature regimes can be identified with those of metallic glasses, spin glasses, and polycrystalline alloys. In addition, Al-*M* quasicrystals can have an unusual Q^{-1} which varies linearly with *T* between 5 and 100 K, a feature not found in either metallic glasses or metals with defects. X-ray diffraction and electron microscopy show no evidence by which to distinguish these quasicrystals. From our measurements we draw three conclusions and suggest what further work on quasicrystals and glasses would be most useful.

The experiments show that the best quasicrystals (from the Al-Li-Cu family in this study) resemble annealed polycrystals much more than they resemble metallic glasses, although we have measured elastic signatures in metastable quasicrystals that are similar to those seen in amorphous metals. A comparison of Bragg peak widths versus phason momentum in melt-spun Al-Mn-Si and faceted dendrites of Al-Li-Cu,⁴⁰ on the other hand, shows no significant difference in the degree of phason strain between these two kinds of alloys. Hence, results like the factor of 5 difference in internal friction at 1 K between Al₇₈Cr₁₇Ru₅ and Al₅₇Li₃₃Cu₁₀ are not due to differences in phason disorder between these two alloys. Although Birge et al.¹ find evidence that the TS density of states in samples of Al-Li-Cu produced by different techniques increases with the degree of phason strain in these samples, our work shows that other factors are of at least equal magnitude when making comparisons between quasicrystals of different families. A second conclusion, following from the glasslike properties of alloys like Al₇₉Ru₂₁, is

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that the disorder specifically responsible for the universal features of glasses must be local and involve only a tiny fraction of the atoms of a disordered solid; a substantial disturbance of the long-range order of a solid is not required to produce these features. Third, quasicrystals have at least one unusual physical property which distinguishes them from crystals and metallic glasses: some of the metastable quasicrystals have an exceptionally large internal friction which increases linearly with temperature between ≈ 5 and ≈ 100 K.

It is interesting to consider how the difference in the internal friction of the stable and metastable alloys might be related to their differing growth kinetics. Measurements of other physical properties of quasicrystals have almost always led to results in which quasicrystals appear to be unremarkable alloys. Unusual elasticity data such as ours are thus sensitive tests of the models of structure and nucleation of quasicrystals; a good theory should account for the substantial differences between Al-M and Al₅₇Li₃₃Cu₁ quasicrystals.

Further progress in the more general problems of disordered solids requires developing a testable theory of the microscopic origin of TS and their relation to disorder and metastability. Quasicrystals, along with recrystallized metallic glasses, can help establish the kind and degree of disorder required to reproduce the properties of fully amorphous materials, and hence constrain models of TS origins in a way that is not possible with the usual glasses. As research move towards explaining the common properties of glasses in the intermediate temperature regime (5 to 100 K), it will also be necessary to examine how the linear variation with T of $\delta v / v$ noted by Bellessa^{26,27} arises as a crystalline alloy is varied in composition from a defect-free crystal to a disordered or metastable metal. In this program, quasicrystals may live up to their promise as a system which links crystals with glasses.

ACKNOWLEDGMENTS

We are pleased to acknowledge Bobby Pohl, Watt Webb, Paul Heiney, and Neil Zimmerman for guidance in matters metallurgical and amorphous; Veit Elser and Chris Henley for stimulating theoretical discussion; and Bud Addis, Maura Weathers, and Ray Coles for invaluable assistance in sample preparation and characterization. This work was supported by the National Science Foundation (NSF) through the Cornell University Materials Science Center, and by Grant No. DMR-84-14796 to W. W. Webb. One of us (K.K) was supported by the Deutsche Forschungsgemeinschaft (Bonn, Germany) Grant No. Kn234/2-1. Two others (N.A.G. and P.A.B.) were supported in part by IBM. The latter (P.A.B.) was also supported in part by the NSF Materials Research Laboratory (MRL) Program and Contract No. DMR-82-16718 to P. Heiney.

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